CARBONIZATION OF COAL-TAR PITCH DEHYDROGENATED BY SULPHUR

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Dehydrogenation of coal-tar pitch with sulphur influences the behaviour of pitch in subsequent carbonization. The carbon yield gets up and chemorheological property changes. Conditions for mesophase formulation are worse because of an increasing viscosity. In extreme case the solidification is done during the dehydrogenation by sulphur. We can control anisotropy and mechanical properties of carbonizates whereby sulphur modification of pitch.

INTRODUCTION

Coal-tar pitch is often used as a relatively inexpensive precursor for preparation of the matrices of carbon-carbon composite materials. The release of low-molecular components in the first phase of the process of pitch carbonization reduces significantly the amount of the carbonization residue. For this reason, it is of advantage to work under an increased pressure which prevents the evaporation of the low-molecular components before the solidification [1]. Before the carbonization proper the pitch may be also subjected to thermal treatment. When heated to relatively low temperature (400 °C), pitch undergoes structural changes. Reaction products with a higher molecular mass are formed which differ in their solubility from the original pitch. In the literature experiments are described which indicate that e.g. by heating the pitch component soluble in toluene to the temperature of 350 - 450 °C substances insoluble in toluene are formed which belong already to the pyridine insoluble or even, to the quinoline insoluble fraction [2]. The same result, although at a lower temperature and within a shorter reaction time, is obtain of case that a suitable catalyst is applied. In dehydrogenation cyclizations e.g. aluminium chloride or alkali metals are used, the yields, however, are not too high [3,4]. Better results were obtained in the dehydrogenation with sulphur. In this case, hydrogen is not released in elemental form but as hydrogen sulphide. The starting temperature of H_2S releasing is approximately 180°C [5].

The effect of sulphur on the pyrolysis of pitch was discussed by Fitzer [6,7]. It was found the relative efficiency of the increase of carbonization residue decreases with the increasing mean molecular mass of pitch. There are two types of prevailing reactions of sulphur with substances contained in pitch. After an addition of up to 7 atom% dehydrogenation reactions of cycloaliphatic molecules prevail. These reactions are terminated at the temperature of 200 - 270 °C and cause a considerable increase of the carbonization residue without limiting the possibility of the subsequent graphitization [6]. In case that a surplus of sulphur is used, the cross-linking of the aromatic molecules with sulfide bridges takes place to a greater extent. These bridges are very stable at high temperature (they decompose only at a temperature around 1000 °C and they may be one of the cause so called puffing during the graphitization. In a similar way as sulphur also amorphous selenium is acting. The latter may be used in a surplus as it does not become part of the molecule. However, the dehydrogenation with selenium takes place at higher temperatures (250-350 °C) [5]

This communication deals with the effect of the modification of commercial electrode coal-tar pitch with elemental sulphur on the course of the carbonization. The purpose of optimum conditions suggested for carbonization is to obtain a carbonization residue as high as possible and such an optical texture of the matrix which would contribute to the improvement of the mechanical properties of the composite.

EXPERIMENTAL PART

The electrode pitch filtered under pressure (215 - 220 °C, 0.4 MPa, inert gas N_2), with the basic properties given in Table I, was mixed with powdered sulphur in the ratios given in Table II.

Table I. Propeties of filtered electrode pitch

Ash	0.04	(wt.%)
H	4.43	-
C	91.64	-
S	0.34	-
N	0.99	-
O	2.60	-
Volatile matter	55.08	-
Non-volatile matter	44.92	-
Softening point (ring-ball)	116.5	(°C)

Table II. Data of elemental analysis (wt.%)

S added	C0	C1	C2	H0	H1	H2	S0	S1	S2
0	91.60	91.61	97.45	4.43	4.43	0.65	0.34	0.34	0.16
1.72	90.02	92.28	97.39	4.35	4.12	0.60	2.05	0.68	0.39
3.14	88.72	93.78	97.16	4.29	4.12	0.47	3.47	0.97	0.47
3.67	88.24	91.98	96.73	4.27	4.04	0.53	4.00	1.08	0.59
5	87.02	92.03	96.30	4.21	3.80	0.58	5.32	1.35	0.70
6.47	85.67	90.60	95.10	4.14	3.38	0.58	6.74	1.52	0.90
10	82.44	91.11	93.67	3.99	3.49	0.44	10.31	2.58	1.17
15	77.86	88.10	92.74	3.77	3.45	0.36	15.29	5.72	2.29
20	73.28	84.00	91.80	3.54	3.14	0.28	20.27	10.81	5.18

X0 - original mixture; X1 - mixture reacted with sulphur at 200 and 270 °C; X2 - mixture after carbonization 950 °C

The samples were melted, mixed and subjected to the thermal regime: 200 °C (2 h) + 270 °C (2 h). The mixtures treated in this way were carbonized under the following thermal regime: 20 - 250 °C (70 °C h^{-1}, 250 - 500 °C (30 °C h^{-1}), 500 - 950 °C (70 °C h^{-1}), 950 - 20 °C (-100 C h^{-1}).

Elemental analysis (C, H, S) of the original pitch, the reacted mixtures and the resulting chars was performed by using the Perkin - Elmer device. Thermogravimetry of reacted samples was performed in the atmosphere of nitrogen with heating rate of 300°C/h up to temperature 950 °C. The optical texture of the carbonization products were determined on polished sections in oil immersion (microscope UMSP 30 Petro from Opton-Zeiss).

RESULTS AND DISCUSSION

The compositions of the mixtures before the reaction, after the reaction with sulphur and after the carbonization are presented in Table II. There is practically no decrease in mass of the pitch proper when heated to 200 and 270 °C. This is in agreement with our expectation as the pitch has been filtered at the temperature of 215 - 220 °C therefore the most volatile components have been released already earlier. The addition of sulphur leads to reactions in which hydrogen sulphide is released. In the course of this process a decreasing the mass of the mixture takes place. This decrease depending on the amount of the sulphur added.

On the basis of the data of elemental analysis and mass losses the decrease in C, H and S in the form of mole fractions related to the quantities of the respective substances in the original mixture were calculated. In Figure 1 these parameters are plotted against added sulphur.

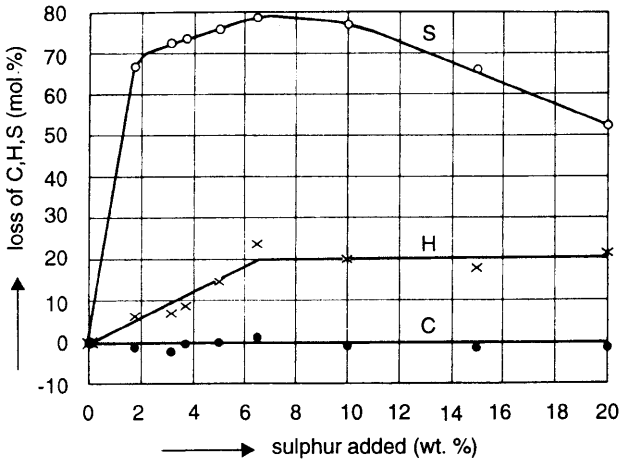

Figure 1. Loss C, H and S after reaction with sulphur

It is evident that during the reaction of the pitch with sulphur no decrease in carbon takes place. The hydrogen content decreases with the amount of sulphur up to approximately 6.5 wt.% and does not exhibit nearly any changes afterwards. The relatively decrease in sulphur exhibit here a maximum (80 % of the sulphur added takes part in the reaction).

The results of thermogravimetry are presented in Figure 2. The curve corresponding to sulphur alone is presented here for comparison. From the figure it follows that the residue after carbonization increases with the amount of sulphur added. The mass residues after the reaction with sulphur and after carbonization are given in Table III. In column *a*) the carbonization residue is related to the original mass of the reacted mixture in question. The major part of the decrease in mass is caused by the decrease in sulphur which is released in the form of H_2S on one hand and which sublimes on the other. When relating carbonization residue to the original quantity of the pitch, we obtain the values presented in the column *b*). So whereas by the carbonization of 100 g of the pitch without added sulphur we get less than 50 g of the product, by the addition of sulphur up to 80 g of char may be obtained from the same quantity of pitch. However, the quality is different: in the case of chars

with sulphur added a part of the sulphur remains in the product (see Table II). There is also a difference in the optical texture. Carbonizates obtained from the neat pitch exhibit a significant amount of optical anisotropy. Fiber and domain textures prevail. However, the fraction of the fiber texture decreases with increasing amount of sulphur and the domain, mosaic and isotropic textures appear in dependence on the increasing amount of sulphur (see Figure 3).

formed by carbonization of the pitch with a low content in sulphur (up to approximately 2 wt.%) fiber textures are typical. The domain texture prevails with carbonizates with the addition of sulphur of about 4 wt.%. For products with a sulphur content of around 7 wt.% mosaic textures are typical. With the sulphur content above 10 wt.% already an isotropic char is obtained. The photographs of the polished sections of typical textures are in the Figures 4-7.

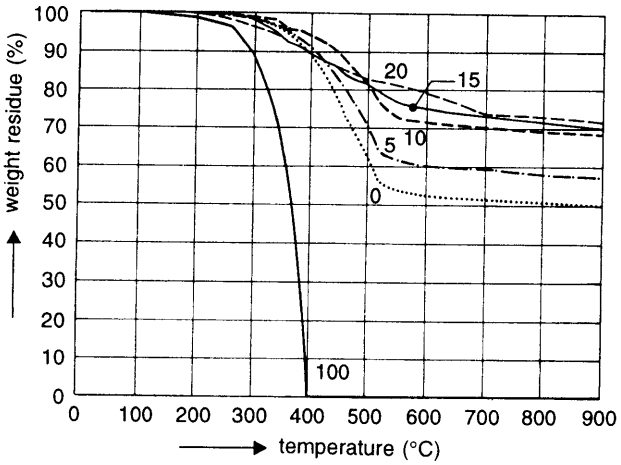

Figure 2. Thermogravimetry of pitch mixtures with sulphur (Heating rate 300 °C h^{-1})
The numbers at the curves indicate the quantity of sulphur added in wt.%, 100 being sulphur alone

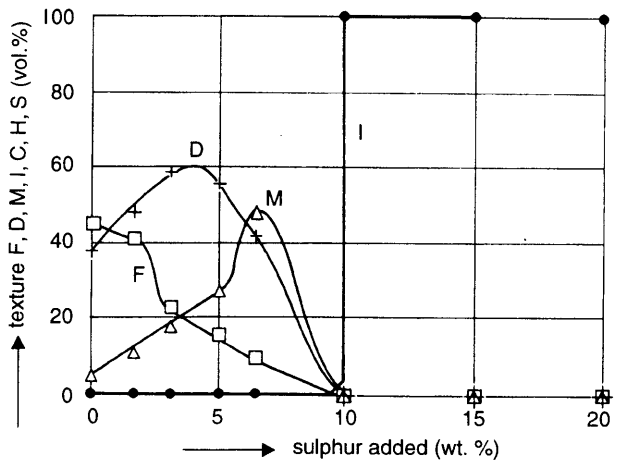

Figure 3. Changes in the texture of carbonizates in dependence on the quantity of sulphur added. (I - Isotropic, M - Mosaic, D - Domain, F - Fiber texture)

Table III. Weight residue after reaction of pitch with sulphur and carbonization (wt.%)

Sulphur (wt.%)	D_1	D_2	D_3
0	100	49.5	49.5
1.72	99.1	51.1	51.5
3.14	97	55.7	55.8
3.67	96.5	56.6	56.7
5	94.7	57.2	57
6.47	93.5	59.9	59.9
10	91.7	68.5	69.8
15	90	69.9	74.1
20	88.7	71.7	79.5

D_1 - weight residue after reaction with sulphur; D_2 - weight residue after carbonization; (related to weight of dehyddrogenated pitch); D_3 - weight residue after carbonization (related to the weight of original pitch)

With a certain simplification we may say that there exist characteristic textures which prevail at a given composition of the mixture pitch-sulphur. For products

In order to determine the total effect of anisotropy the optical texture indexes OTI for samples were calculated. In Table IV we see the decrease in the anisotropy of the carbonizates with the increasing amount of sulphur added.

The changes in the texture may be interpreted by the change of the carbonization conditions. The formation of mesophase is conditioned by certain requirements on the precursor and the carbonization process. First of all, the molecules must have a suitable size-a molecular mass around 900 is specified [8]. The system must exhibit at the temperature of mesophase formation (400 - 450 °C) a low viscosity for a sufficiently long time so that the molecules can arrange themselves into liquid crystals. On the other hand, materials with too high viscosity form an isotropic carbon during thermal treatment. For example, cross-linked polymers carbonize in this way. However, systems which were not cross-linked originally, the reactivity of which under conditions given is too high, may cross-link sooner then the mesophase will time enough to be formed [9]. Anisotropic structures are typical for the products obtained by the carbonization of pitch. However, by modifying the pitch prior to the car-

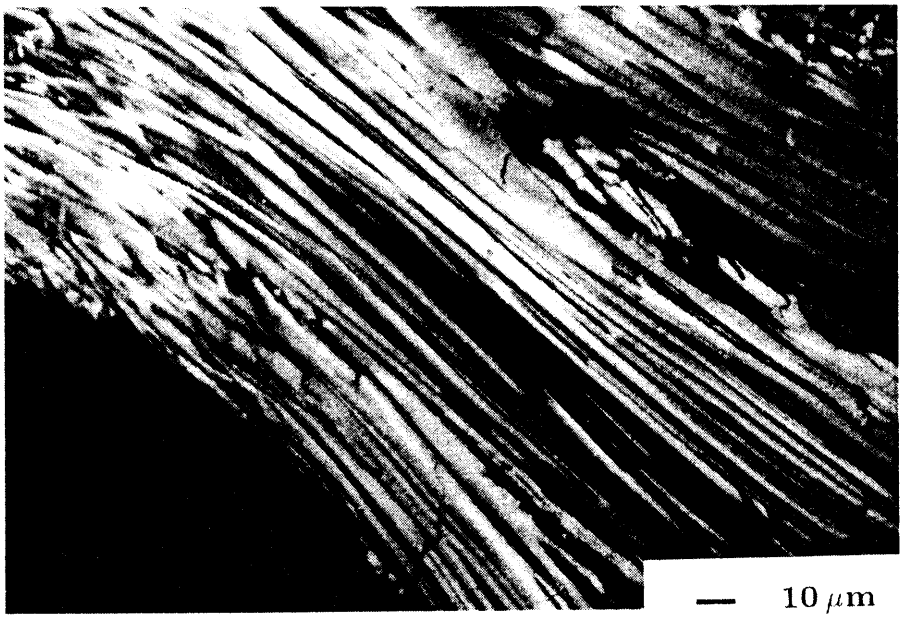

Figure 4. Typical texture of carbonizates (0 wt.% S)

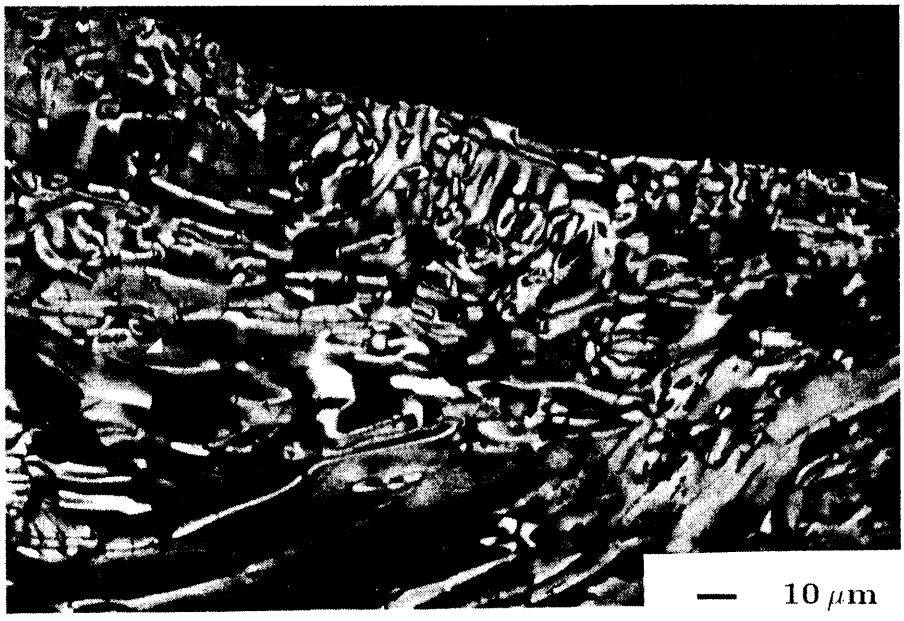

Figure 5. Typical texture of carbonizates (3.14 wt.% S)

bonization proper we affect its chemorheological behaviour. The viscosity of the mixtures with sulphur increases significantly after the reaction. The samples with sulphur content of up to 6,47 wt.% could still be melted, the sample with 10 wt.% did not melt any more after reaction, it only softened. Pitch mixtures containing more then 10 wt.% sulphur delivered a glassy non-melting substance. The solidification of samples with 10 and

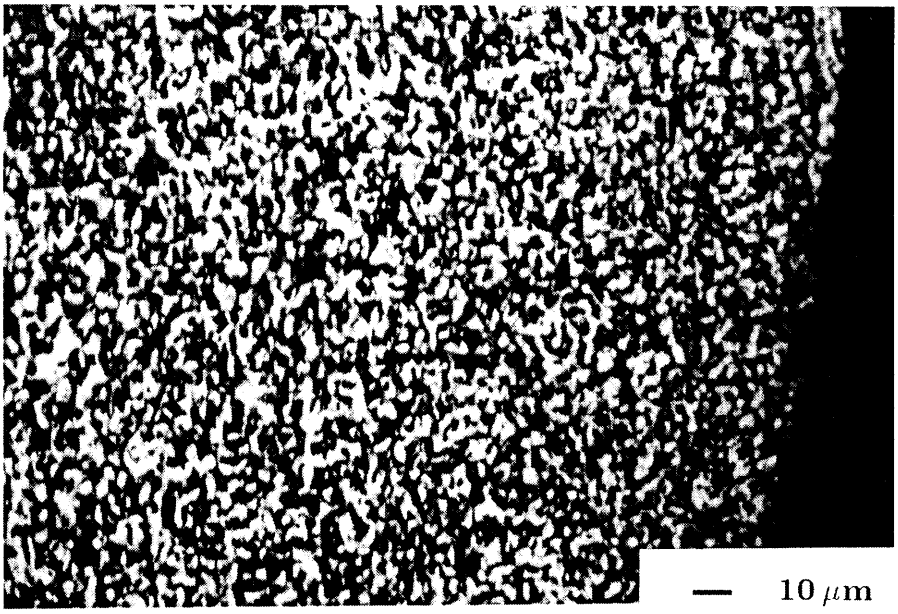

Figure 6. Typical texture of carbonizates (6.47 wt.% S)

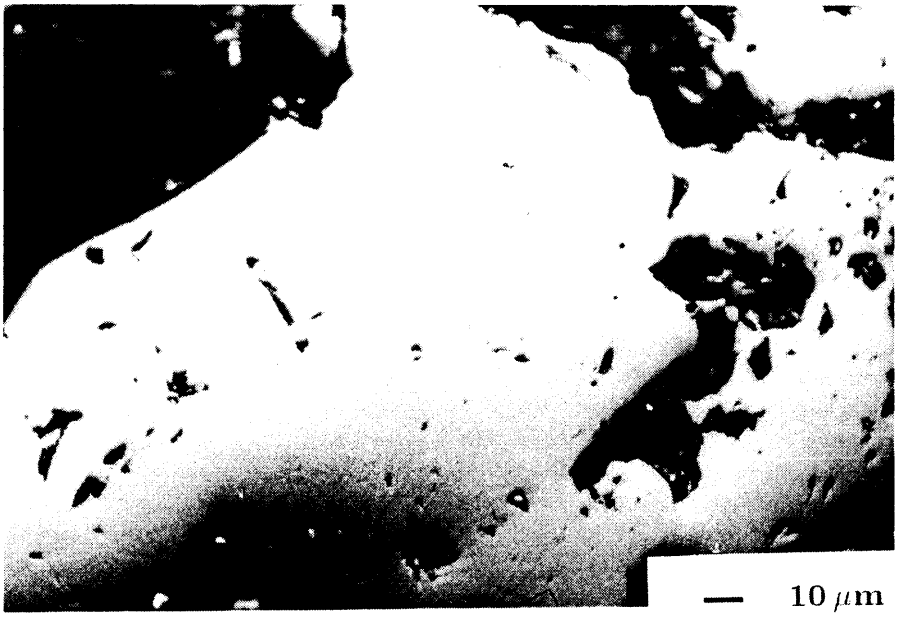

Figure 7. Typical texture of carbonizates (10 wt.% S)

more wt.% sulphur takes place already during the reaction with sulphur at the temperature of 270 °C. In the course of the carbonization intermediate products of this type do not melt any more so that no formation of a mesophase may take place. The result is then isotropic carbon which is typical for carbonization of cross - linked polymers.

Table IV. Optical texture of carbonized mixtures (vol.%)

sulphur added (wt.%)	0	1.72	3.14	5.00	6.47	10.00	15.00	20.00
Isotropic	0	0	0	0	0	0	0	0
Mosaic								
smooth	0	2	7	9	10	0	0	0
middle	1	9	9	9	11	0	0	0
corse	4	0	2	9	27	0	0	0
total	5	11	18	27	48	0	0	0
Domen								
smooth	14	10	20	27	17	0	0	0
middle	16	18	14	11	10	0	0	0
corse	8	20	25	18	15	0	0	0
total	38	48	59	56	42	0	0	0
Fiber								
short	24	18	10	7	4	0	0	0
long	21	23	13	9	6	0	0	0
total	45	41	23	16	10	0	0	0
IOT	18.0	13.0	12.5	10.9	9.5	0	0	0

CONCLUSION

In the carbonization of pitch under atmospheric pressure the residue after the carbonization is relatively low (around 50 wt.%). this is caused mainly by the release of low-molecular components prior to the solidification. One of the possibilities how to increase the carbonization residue is the preliminary dehydrogenation of the pitch with sulphur. In this way the carbonization residue may be increased nearly up to 80 wt.%, however, only at the cost of a changed structure of carbonizate which manifests itself among other effects in the optical texture. The various types of pitch in the carbonization usually give products with anisotropic textures. The dehydrogenation with sulphur prior to the carbonization affects the chemorheological behaviour of the pitch. With the increasing amount of sulphur the conditions for the formation of anisotropic particles worsen as the viscosity of the pitch increases considerably. In the extreme case the solidification takes place already during the reaction with sulphur. In the course of the carbonization proper the intermediate product does not melt any more and no arrangement of the molecules into the structure of liquid crystals can take place. An anisotropic material of the types of glassy carbon is formed, as it is usual in the carbonization of cross-linked polymers. Therefore, by modifying the pitch with sulphur, we may control the anisotropy of the carbonizate and thus also its mechanical properties. The aim of the ensuing investigation will be to examine the effect of this optical texture on the mechanical properties of carbon - carbon composite materials [10].

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KARBONIZACE ČERNOUHELNÉ SMOLY DEHYDROGENOVANÉ SÍROU

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Dehydrogenace černouhelné smoly sírou v množství do 20 % ovlivní chování smoly při následné karbonizaci. Zvýší se zbytek po karbonizaci až o 20 hmotnostních % a ovlivní se též chemoreologické chování smoly. Se zvyšujícím se podílem síry se zhoršují podmínky pro vznik anizotropních, částic neboť viskozita smoly výrazně stoupá. V krajním případě dojde k solidifikaci již během reakce se sírou. Při vlastní karbonizaci se meziprodukt již neroztaví a k uspořádání molekul do struktury kapalných krystalů nemůže dojít. Vzniká izotropní materiál typu skelného uhlíku, tak jak je to obvyklé při karbonizaci síťovaných polymerů. Modifikací smoly sírou můžeme tedy řídit anizotropii karbonizátu a tím i jeho mechanické vlastnosti. Materiál bude dále zkoušen jako matrice pro kompozity uhlík - uhlík.